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Removal of Glyphosate from Drinking Water

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16. ABSTRACT

The effectiveness of GAC, PAC, conventional treatment, membranes, and oxidation for removing glyphosate from natural waters is evaluated. Results indicate that GAC and PAC are not effective in removing glyphosate, while oxidation with chlorine was very effective.

granulated activated carbon

powdered activated carbon

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THE REMOVAL OF GLYPHOSATE FROM DRINKING WATER

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INTRODUCTION

Glyphosate is a non-selective, broad-spectrum, post-emergent herbicide that is to be regulated by the Safe Drinking Water Act (SDWA). Glyphosate is zwitterionic with pK_a values of <2.0, 2.6, 5.6, and 10.6 as determined by Sprankle et al. (1). Figure 1 shows the dissociation species. As can be seen, glyphosate displays amphoteric character with its phosphonate, carboxyl, and amine groups. Glyphosate is nonvolatile. Its herbicidal activity comes from its inhibition of the 5-enolpyruvylshikimic acid-3-phosphate synthase which normally leads to the biosysthesis of aromatic amino acids (2).

A great deal of work has been completed which shows that glyphosate associates with metals. Sprankle et al. (1) found that the binding of glyphosate to clays and soils did not relate to the cation exchange capacity of the material, but rather the cations on the material. The binding of glyphosate to cation-saturated organic matter increased in the following order: $Na^{+} = Mg^{+2} < Zn^{+2} < Ca^{+2} = Mn^{+2} = Fe^{+3} = Al^{+3}$. Whereas cation-saturated clays increased in the following order: $Ca^{+2} < Mn^{+2} < Zn^{+2} < Mg^{+2} < Fe^{+3} < Al^{+3}$. Hensley et al. (3) also showed that glyphosate chelated with metals associated with soil. Shoval and Yariv (4) and McConnell and Hossner (5) determined that glyphosate/metal complexes were formed within the inner layer of the clays that they studied. They determined that the most likely complexation mechanism was a water-bridge between the carboxylic and phosphonic acid groups and the exchangeable cations on the clay. Subramaniam and Hoggard (6) also found that glyphosate chelates with metals. Sprankle et al. (1) and Hance (7) found that the adsorption mechanism for glyphosate and inorganic phosphate were similar, however, the inorganic phosphate adsorbed preferentially.

Previous researchers (8-12) have shown that very hydrophobic compounds complex with natural organic matter. However, the above findings concerning the possibility of a organic/metal/glyphosate complex is different than the organic/compound complexation found with very hydrophobic compounds. Previous researchers have indicated that a compound's octanol/water coefficient can be used to determine if a compound is likely to associate with natural organics (8,12). Other researchers have correlated octanol water coefficients with solubility (8,12-15). Using these two types of correlations, glyphosate was determined to be unable to complex appreciably to organic matter by a hydrophobic mechanism.

Complexation with natural species is an important topic because the resultant species may exhibit different treatment characteristics than the unbound contaminant. This paper attempts to test the effectiveness of various treatment processes on glyphosate, and looks into whether the complexation phenomena may be affecting the results.

METHODS AND MATERIALS

Glyphosate was analyzed by a high performance liquid chromatography method with post-column derivatization. The waters used were either distilled water or Ohio River water. Water from the Great Miami Aquifer was also used initially, but it was found that glyphosate degraded quickly in it. This was not surprising because other researchers have found that decomposition rates in natural systems vary widely (16).

The isotherm procedure used 100x200-mesh F-400 (Calgon Corp.) carbon and 250 ml PTFE-capped glass bottles. The isotherms were equilibrated in an end-over-end tumbler for three weeks. The procedure is identical to that published earlier (17).

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Figure 9. Gamma Exposure Rate Values for Block #4-II 10/11/89- 18 hr After Removal From Service

The microcolumns used 100x200-mesh F-400 carbon and were 0.4 cm in diameter. The loading rate was a nominal 30 gpm sq ft, and the empty bed contact time (EBCT) was a nominal 0.06 minutes. The scale-up method used was based on the work of Crittenden (18) which assumes a constant surface diffusivity with particle size. The microcolumn conditions scaled to a 12x40-mesh full-scale reactor with a nominal loading rate of 3 gpm/sq ft and a nominal EBCT of 5 minutes.

The pilot column used 12x40-mesh F-400 carbon and was 1.5 inches in diameter. The loading rate was a nominal 2 gpm sq ft, and the EBCT was a nominal 5 minutes. The microcolumn and pilot-column procedures are identical to what has previously been published (19-20).

The jar tests were run to simulate full-scale coagulation, flocculation, and sedimentation processes. Jar-test equipment and procedures described by Hudson (21) and Miltner et al. (22) were employed. Alum was used as the primary coagulant. The alum doses were between zero and 40 mg/L depending on the test run. In some cases, a cationic, anionic, or nonionic coagulant aid was used. The polymers were dosed between zero and 1 mg/L. A certain number of the runs employed powdered activated carbon (PAC). The carbon used was WPH (Calgon Corp.) with doses ranging from zero to 50 mg/L. The coagulant, coagulant aids, and PAC were added during the rapid mixing which was set for 100 rpm for 2 minutes. The subsequent flocculation and sedimentation mixing speeds were: 30 rpm for 10 minutes, 20 rpm for 10 minutes, 10 rpm for 10 minutes, and 0 rpm for 60 minutes. At the end of sedimentation; turbidity, temperature, pH, and contaminant samples were taken. In the case of the distilled-water jar tests with PAC addition, a 0.45-micron filter was used after the settling time to remove the suspended PAC.

Amicon ultra-filtration membranes were used to fractionate the water into different molecular weight fractions in an attempt to determine if glyphosate formed organic/metal/glyphosate complexes. The molecular weight cut-offs of the membranes were 100,000; 1,000; and 500. The ultra-filtration membranes were 76 mm in diameter and were used in a standard Amicon cell. A nitrogen atmosphere of 50 psi was used to pass the water through the membrane. A 0.45 micron filter manufactured by Millipore was used for a micro-filtration study. A sand column run at 0.15 gpm/sq ft was used to study slow-rate filtration. The sand column was 2 feet deep and was composed of filter sand.

The oxidations studies were run with chlorine, chlorine dioxide, hydrogen peroxide, and permanganate. The doses in mg/L were 3.0, 1.0, 1.0, and 1.0, respectively. The solutions were in contact with the oxidant for 15 minutes before thiosulfate was added to quench the reaction. The chlorine stock was prepared from commercially available calcium hypochlorite. The chlorine dioxide stock was prepared according to standard methods (23). The hydrogen peroxide stock was prepared from a commercially available solution. The permanganate stock was prepared from potassium permanganate crystals. Chlorine and chlorine dioxide were quantified by the DPD method (23). Hydrogen peroxide and permanganate were not quantified.

DISCUSSION

Figure 2 shows the distilled-water and Ohio-River-water isotherms for glyphosate. As can be seen, there was a large difference between the isotherm capacities of glyphosate in distilled water and Ohio River water. In distilled water, glyphosate was very strongly adsorbed. In Ohio River water, it was much more weakly adsorbed. The microcolumns shown in Figure 3 show the same effect. The breakthrough profile for the distilled-water microcolumn indicates that the kinetics of adsorption of glyphosate are very slow. Table 1 shows the capacities of the adsorption studies. Because the distilled-water microcolumn was clearly not at equilibrium, the ultimate capacities in the distilled-water isotherm and microcolumn may have been similar. The Ohio-River-water isotherm and microcolumn results do not indicate this so clearly because the microcolumns appeared to be quite close to complete breakthrough. This suggests that the natural organics, and possibly metals, in the Ohio River water interfered with the adsorption of glyphosate, and this interference was mechanistically different between the batch isotherm and the flow-through column.

The large difference between capacities of the Ohio-River-water tests and the distilled-water tests may be due to a number of factors. To show that the effect of the raw water in reducing the capacity of glyphosate was greater than that expected by normal competitive adsorption, a hypothetical component of the Ohio-River-water background using the Ideal Adsorbed Solution Theory (24-25) was found for glyphosate by comparing the distilled-water and Ohio-River-water isotherms. Crittenden et al. (26) has previously used this technique for natural-water systems. The results for glyphosate were then compared to hypothetical components for the Ohio-River-water background for a number of other compounds which have had isotherms completed in both distilled and Ohio River water. The isotherms used in this procedure have previously been published by Speth and Miltner (17). The hypothetical component's Freundlich 1/n, concentration, and molecular weight were arbitrarily set in all cases at 0.3, 2.4 mg/L, and 100, respectively. This was so that only the Freundlich K needed to be adjusted to fit the Ohio-River-water isotherm. By comparing the resultant Freundlich K's, the relative adsorption strengths of the background for each compound's Ohio-River-water isotherm could then be compared. The results are presented in Table 2. As can be seen, the organic background for the glyphosate isotherm was determined to be so strongly adsorbed that regardless of how high the Freundlich K of the hypothetical component was adjusted, the IAST prediction did not fit glyphosate's Ohio-River-water isotherm. The Freundlich K for the hypothetical components for the other compounds could all be quantified. These results imply that the adsorption of glyphosate in Ohio River water could have been influenced by complexation as discussed above, or by an extremely slow adsorption rate for glyphosate that allowed the natural organics in the water to preload, or foul, the carbon before the glyphosate was fully adsorbed. Other compounds such as alachlor, pentachlorophenol, and aldicarb showed a slightly higher hypothetical component. This could be due to a hydrophobic complexation mechanism which is possible because these compounds were some of the most hydrophobic on the list.

Table 3 contains a carbon use rate for a pilot column fed glyphosate-spiked Ohio River water. Because of glyphosate's slow adsorption kinetics, the pilot column was only run to 20 percent of breakthrough. Therefore, the carbon use rate is the carbon used per 1000 gallons treated to achieve 20 percent breakthrough. Also listed in Table 3 are the constant-pattern-homogeneous-surface-diffusion model (CPHSDM) predictions using both distilled-water and Ohio-River-water capacities and various adsorption kinetic rates. The CPHSDM was developed by Hand et al. (27). According to Crittenden et al. (28), the CPHSDM with a kinetic flux ratio (surface-to-pore-diffusion-flux ratio) of 3.72 with a distilled-water isotherm capacity will define breakthough in a granular-activated-carbon (GAC) column which is fed distilled water. Crittenden et al. (28) also stated that a kinetic flux ratio of 0.4 with a distilled-water isotherm capacity will define early breakthough a GAC column fed a natural water. Ford et al. (29) found that the combination of a kinetic flux ratio of 3.72, a distilled-water isotherm capacity, and a natural-water adjustment factor was a good predictor of breakthough in GAC columns fed natural waters. This last method was used in the Cost and Technology document which supports the SDWA (29). Also shown on Table 3 is a CPHSDM prediction with a kinetic flux ratio of 0.4 and an Ohio-River-water isotherm capacity. This prediction is the worst case scenario in terms of modeling kinetics and capacity. As can be seen, all of the carbon use rate predictions are much lower than the pilot-column results. Even the prediction with the very slow adsorption kinetics and the Ohio-River-water isotherm capacity is not even one-half of the actual carbon use rate. These results are consistent with the conclusion gathered from the microcolumn work which suggested that glyphosate has very slow adsorption kinetics or has the ability to form weakly-adsorbing organic/metal/glyphosate complexes. Whichever the case, these data show that a compound can be strongly adsorbed as a single solute, but weakly adsorbed in a natural water hence leading to a wrong modeling conclusion regarding the effectiveness of GAC treatment.

Figure 4 shows the results for a series of alum-coagulated jar tests some of which used coagulant aids. As can be seen, the concentration of glyphosate dropped sharply from approximately 2500 ppb to near zero as the turbidity fell from 2 NTU to near zero. The same trend was evident, as shown in Figure 5, when glyphosate was spiked at a lower concentration (75 ppb). The type of coagulant aid had no direct bearing on glyphosate removal, but did increase floc size and settling velocity hence creating finished waters with higher turbidities than generally found with alum. Jar tests in distilled water with alum as a coagulant showed no glyphosate

removal. Also, the glyphosate removal in the Ohio-River-water jar tests did not correspond to alum dosage. These results indicate that glyphosate was not being removed by alum alone, but rather by the alum/organic floc. This is entirely consistent with the previous researchers who have suggested that glyphosate forms organic/metal/glyphosate complexes (1, 3-5).

Jar-test studies with PAC addition showed that the carbon had no effect on glyphosate removal levels in Ohio River water. Even in distilled water with no coagulant, there was very little removal. The distilled-water results showed that for a nominal 50 mg/L dosage of WPH carbon, there was a 12 percent removal of glyphosate. This was much lower than expected, and indicates that the adsorption kinetics for glyphosate are extremely slow. This is consistent with the microcolumn and pilot-column tests which also suggest that the adsorption kinetics for glyphosate are very slow. The lack of removal of glyphosate in Ohio River water could also be due to the very low capacities of glyphosate in natural waters as suggested by the isotherm and microcolumn work.

In an effort to determine if glyphosate forms organic/metal/glyphosate complexes, ultra-filtration membranes of molecular weight cut-offs of 500; 1,000; and 100,000 were used with glyphosate-spiked Ohio River water. Figure 6 shows the results. As can be seen, the 0.45 micron filter and the 100,000 molecular cut-off membrane did not remove the glyphosate even though the turbidity was reduced to below 0.2 NTU. The 1,000 molecular weight cut-off membrane rejected approximately one-half of the glyphosate, while the 500 molecular weight cut-off membrane rejected almost all of the glyphosate.

The fact that the 0.45 micron filter and the 100,000 molecular cut-off membrane did not remove glyphosate even though turbidity was reduced to below the levels that the jar tests determined to be required to see a glyphosate reduction, strengthens the theory that an alum/organic/glyphosate complex was being removed in the jar tests as opposed to a glyphosate/turbidity-matter complex. This matter is further reinforced by the sand-filtration study which showed that for even a flow rates as low as 0.15 gpm/sq ft, glyphosate was not removed.

To determine if the 1000 and 500 molecular weight cut-off membranes were rejecting a complexed molecule and not glyphosate itself, membrane studies with distilled water were completed. The results for distilled water are shown in Table 4. The 1000-MW cut-off membrane removed approximately 80 percent of the glyphosate while the 500 MW cut-off membrane removed all of the glyphosate. Therefore, uncomplexed glyphosate was removed with membranes with molecular weight cut-offs much higher than glyphosate's own molecular weight of 169.7. These results are similar to what was found in Ohio River water as described above. Therefore, the membrane results using Ohio River water do not prove that glyphosate forms organic/metal/glyphosate complexes.

In an attempt to determine if glyphosate's net-negative charge was causing the membranes to reject glyphosate, distilled water spiked with glyphosate was reduced to a pH of 2.0 where glyphosate has a net neutral charge (see Figure 1). In the previous tests, the pH was 7.8 for the Ohio River water and 7.6 in distilled water. The results (Table 4) show that approximately 30 percent of the glyphosate passed the membrane. This is greater than for the high-pH distilled-water study, but it does not prove that glyphosate was rejected because of a charge rejection.

Figure 7 displays the results for an oxidation study with glyphosate-spiked Ohio River water. The results show that glyphosate can be easily oxidized by chlorine. Potassium permanganate and chlorine dioxide were only somewhat successful in removing glyphosate, while, hydrogen peroxide was not effective under the conditions tested. The results are not surprising given that calcium hypochlorite is used in the analytical method to oxidize glyphosate into glycine and phosphonomethyl moieties.

CONCLUSIONS

* There was a large difference between the isotherm capacities of glyphosate in distilled water and Ohio River water.

* The microcolumn, pilot-column, and jar-test studies verified the capacity differences found with the isotherms and showed that glyphosate has extremely slow adsorption kinetics.

* The large difference in distilled-water and Ohio-River-water capacities was not expected from hypothetical component work involving a number of other compounds for which both distilled-water and Ohio-River-water isotherms were available.

* The pilot-column study had carbon use rates that were orders of magnitude greater than what was predicted by state-of-the-art computer models that are used to generate cost figures to support the SDWA. By all indications, glyphosate is a very unique compound in this regard.

* The possibility exists that the natural-water-adsorption findings were the direct result of glyphosate forming glyphosate/organic/metal complexes.

* The jar-test studies found that as turbidity was removed, so was glyphosate. The majority of the glyphosate removal happened as the turbidity was reduced below 2 NTU.

* The glyphosate removal was found to be independent of alum dose suggesting that the organic matter in the alum floc had some role in removing the glyphosate.

* PAC treatment was ineffective in both Ohio River water and distilled water because of glyphosate's slow adsorption kinetics.

* Slow-rate filters, 0.45-micron filters, and 100,000-molecular-weight-cut-off ultra- filtration membranes did not remove glyphosate in Ohio river water even though the effluent turbidity was reduced to below 0.2 NTU which is well below the level indicated by the jar tests to be required to remove glyphosate. This further strengthens the case for a alum/glyphosate/organic removal mechanism in the jar tests.

* For both distilled water and Ohio River water, 1,000-molecular-weight-cut-off membranes rejected approximately 50 percent of the glyphosate, and 500-molecular-weight-cut-off membranes rejected all of the glyphosate.

* 500-molecular-weight-cut-off membranes rejected a large percentage of the glyphosate in distilled-water at a pH of 2.0.

* The reason for the 500- and 1000-molecular-weight-cut-off membrane rejection of glyphosate is unknown.

* Glyphosate was shown to be easily oxidized by chlorine. Permanganate and chlorine dioxide were only somewhat effective, while hydrogen peroxide was not effective.

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This abstract has not been subject to agency review and therefore does not necessarily reflect USEPA policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the USEPA.

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TABLE 1

Glyphosate Capacities for GAC Studies.

Study	C_e (mg/L)	Q_e (mg g)
Isotherm (distilled water)	2.52	223
Isotherm (Ohio River Water)	2.99	15.5
Microcolumn #1 (distilled water)	2.52	81.5*
Microcolumn #2 (Ohio River water)	2.99	1.70
Microcolumn #3 (Ohio River water)	2.99	0.625

* = Column not yet to equilibrium.

TABLE 2

Freundlich Values for Hypothetical Components Needed to Account for Ohio-River-Water-Isotherm Capacity

Compound	Freundlich K $(\mu g/g)(L/\mu g)^{1/n}$
Alachlor	750
Aldicarb	100
Bromoform	5
Carbofuran	1
Chlorobenzene	10
Chlorobenzene	75
Chloroform	1
Dibromochloropropane	20
1,2-Dibromoethane	0.1
o-Dichlorobenzene	1
1,1,1-Trichloroethane	1
1,1,1-Trichloroethane	1
cis-1,2-Dichloroethene	1
trans-1,2-Dichloroethene	10
1,2-Dichloropropane	1
1,2-Dichloropropane	1
Glyphosate	NA
Lindane	1
Pentachlorophenol	300
Pentachlorophenol	300
Trichloroethene	40
1,2,3-Trichloropropane	10

NA indicates that no Freundlich K would reduce the IAST prediction to the capacity of the Ohio-River-water isotherm.

All hypothetical component have arbitrary 1/n's, concentrations, and molecular weights of 0.3, 2.4 mg/L, and 100, respectively.

More than one isotherm was completed for certain compounds.

TABLE 3

Carbon Use Rates to 20 Percent Breakthrough for Ohio River Water Pilot Column and CPHSDM Predictions

Source		Carbon Use Rate (lbs/1000 gal)
CPHSDM Prediction		
Flux Ratio		
0.4	- distilled water	0.155
3.72	- distilled water	0.074
3.72	- distilled water *	0.207
0.4	- Ohio River water	2.44
Pilot Column Data		
	- Ohio River water	4.90

* denotes that a carbon use rate adjustment factor was applied.

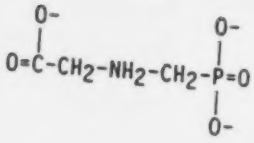
TABLE 4

Fractionation Results for Glyphosate in Distilled Water.

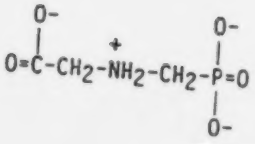
Sample	1000 MW Membrane pH = 7.6		500 MW Membrane pH = 7.6		500 MW Membrane pH = 2.0	
	Volume (ml)	Conc. (mg/L)	Volume (ml)	Conc. (mg L)	Volume (ml)	Conc. (mg/L)
Influent	292[i]	0.643	352[i]	0.643	296[i]	0.913
Effluent	148	0.117	154	0.0	161	0.271
Not Passed	144	1.208	198	1.058	135	1.406

[i] = Initial volume into stirred cell.

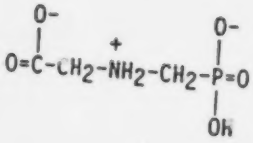
pH above 10.6
Charge = -3



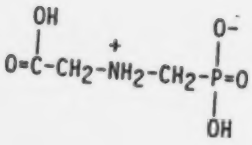
pH between 10.6 and 5.6
Charge = -2



pH between 5.6 and 2.6
Charge = -1



pH between 2.6 and <2
Charge = 0



pH below <2
Charge = +1

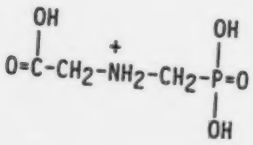


Figure 1. Dissociation species for glyphosate.

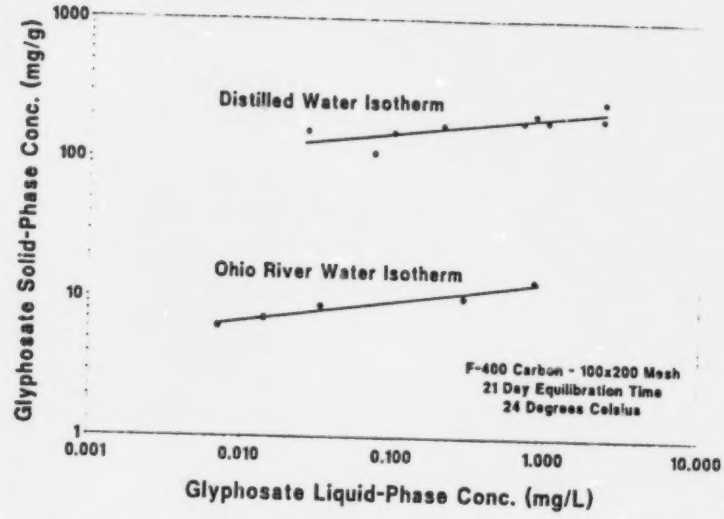


Figure 2. Isotherm Results for Glyphosate in Distilled Water and Ohio River Water.

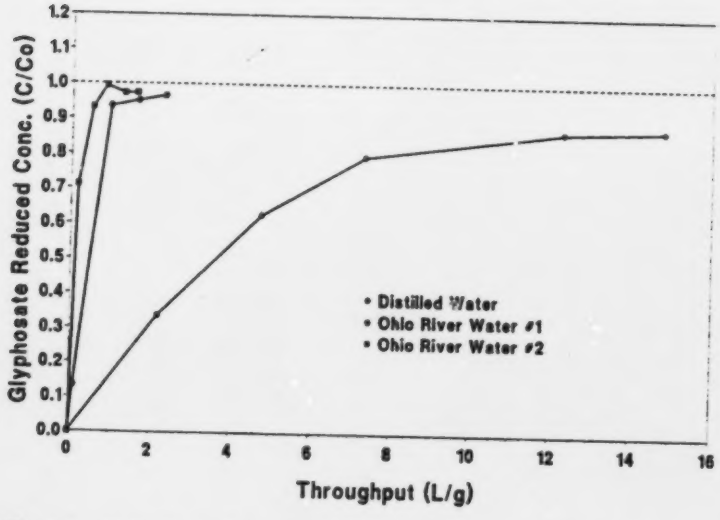


Figure 3. Microcolumn Results for Glyphosate in Distilled and Ohio River Water.

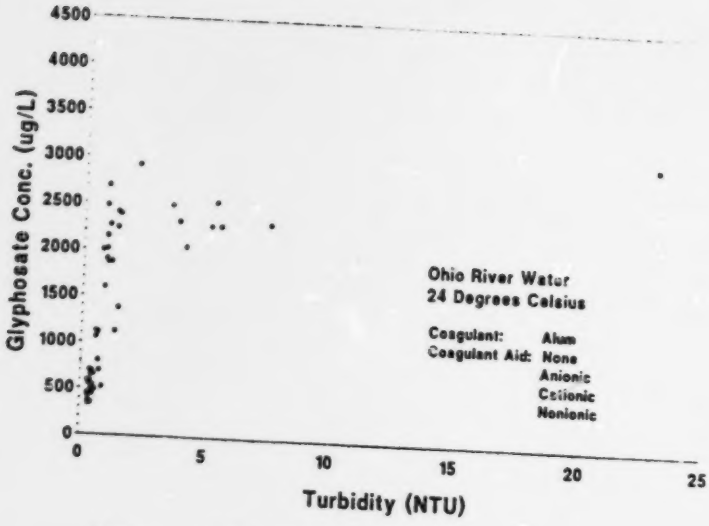


Figure 4. Jar-Test Results for Glyphosate in Ohio River Water.

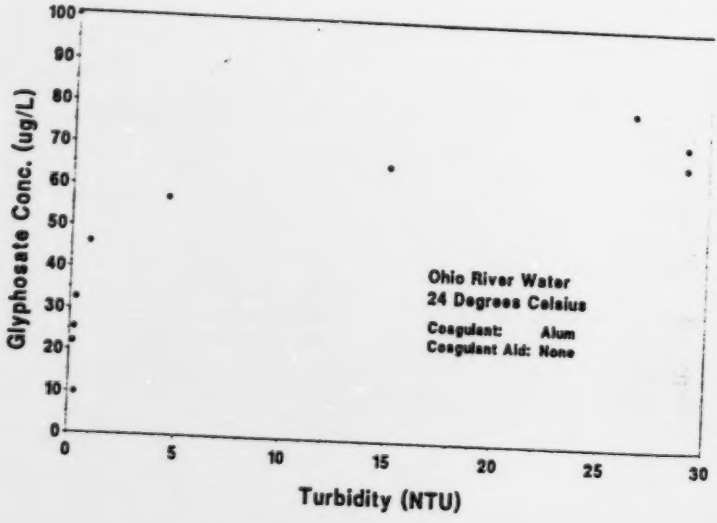


Figure 5. Jar-Test Results for Glyphosate in Ohio River Water.

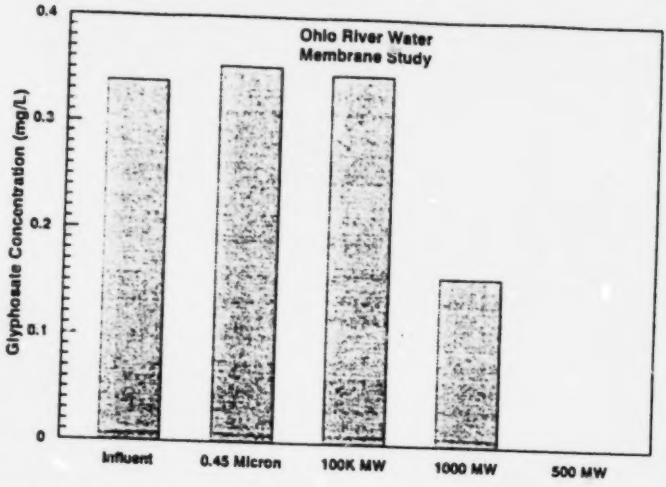


Figure 6. Ultra-Filtration Membrane Study Results for Glyphosate in Ohio River Water.

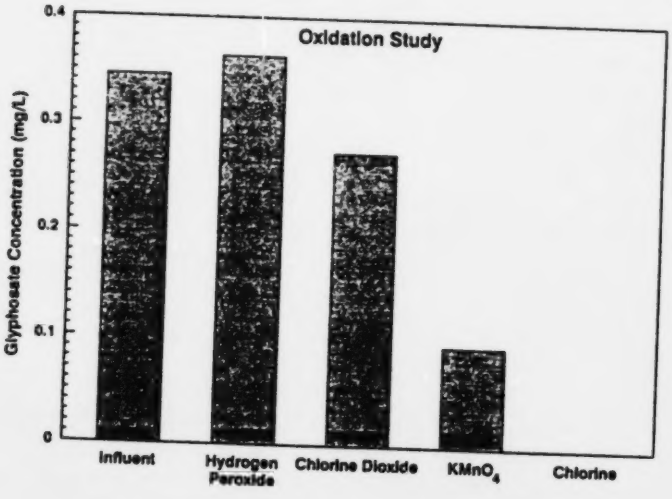


Figure 7. Oxidation Results for Glyphosate in Ohio River Water.